Chemosphere 91 (2013) 838–843

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Dioxins and furans releases in Iranian mineral industries

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HIGHLIGHTS

- Emissions of PCDD/Fs of Iranian mineral industries were investigated and estimated.
- PCDD/Fs emissions from eight major metallurgical and cement plants were estimated.
- Samples from steel plant and cement plant were analysed for PCDD/Fs.
- The dioxins loads of the tested samples are unusually low.
- The result can confirm the necessity and feasibility of sampling gaseous effluents.

ARTICLE INFO

Article history:
Received 6 June 2012
Received in revised form 20 December 2012
Accepted 16 January 2013
Available online 13 March 2013

Keywords:
Cement
Dioxins
Direct reduction
Integrated iron & steel production
Primary aluminium and copper production
UNEP Toolkit

ABSTRACT

In this project, emissions of Poly-Chlorinated Dibenzo-p-Dioxins and Dibenzo-Furans (PCDD/Fs) were investigated and estimated for selected Iranian mining and ore processing industries, such as integrated iron & steel plant, primary production of aluminium and copper metal, and the production of cement. As a first step of this study the annual emission of PCDD/Fs was estimated at 120 g TEQ annum^{-1} on the base of the UNEP standardised Toolkit for identification and quantification of dioxin and furan releases. Steel and cement were identified as major emission sources and earmarked for further scrutiny. For that reason, filter dust arising in these plants was sampled and analysed, as well as all raw materials employed. After extraction and clean-up according to standard methods, the resulting liquid samples were analysed and quantified by HRGC–HRMS. Complementary analyses using methods such as XRF, TGA/DTA were performed and the emission results statistically evaluated, in order to put PCDD/F emissions in perspective. It is concluded that the dioxins load of cement dust is unusually low, following the low carbon in raw materials, the use of natural gas as a fuel and the absence of waste incineration. Also the production of iron by direct reduction of ore is a low dioxins process; dioxin loads in dust are as usual – correlated with the presence of catalytic metals. Loss on ignition and chlorine are anti-correlated with the main earth elements and with sulphur oxides.

1. Introduction

Poly-Chlorinated Dibenzo-p-Dioxins and Dibenzo-Furans (PCDD/Fs), in brief dioxins, form a generic group of 75 PCDD congeners and 135 PCDF congeners (chlorination level $P = 1–8$). Congeners containing up to three chlorine atoms are considered of little toxicological significance. Congeners with chlorine atoms substituted in the lateral 2, 3, 7 and 8 positions of the aromatic rings, however, create substantial health and environmental hazards. Increasing the substitution level from four to eight chlorine atoms markedly decreases dioxins potency, as expressed in Toxicological Equivalence or TEQ units (WHO, 1998).

Dioxins show low vapour pressure, very low water solubility, high octanol/water partition coefficients; they adsorb strongly to particles and surfaces and are resistant to degradation under environmental conditions. Their inherent stability, persistence in the environment and high fat solubility results in lipophilic bio-concentration and accumulation in the food chain. Almost all individual PCDD and PCDF congeners have been identified in emissions from thermal and industrial processes and as a consequence are found in environmental matrices such as soil, sediment, plants, air and water, although their low aqueous solubility also means that they are largely immobile in soils and can hardly be detected in water. Dioxins are trace contaminants in a number of chemical products, e.g. those derived from chlorophenols. They are unintentionally formed in most thermal, metallurgical and combustion processes, mainly between 250 and 450 °C.

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0045-6535
http://dx.doi.org/10.1016/j.chemosphere.2013.01.064

In this study, information from selected industrial Iranian plants is presented and analysed to investigate both the necessity and feasibility of further sampling the actual gaseous effluents. The project is conducted within the frame of the Stockholm Convention on Principal Organic Pollutants (POPs) to which Iran has subscribed; the results from this study can be evaluated against those of the National Inventory (UNEP, 2008).

2. Materials and methods

2.1. Paper study

This study was accomplished in two parts:

(1) Applying the UNEP standardised Toolkit for identification and quantification of dioxin and furan releases to estimate the annual emissions of PCDD/Fs from Iranian mining industries.
(2) Next, the flow sheet of all plants was studied, dust samples were taken at appropriate locations of selected plants, and analysis of tetra-to octa-chlorinated dioxins and furans was performed on the most relevant samples from cement and steel plant by HRGC/HRMS. Dust analysis alone is insufficient to characterise these outputs (the finest dust, eluding collection, might carry a higher load), but the values given in Table 1 already allow appreciating the gravity of emissions and the location of the most important sources of dioxins, further treated anonymously.

First eight major industrial plants were selected within our scope of mining related industries and then the Toolkit questionnaires were prepared and dispatched to the plant operators. The plants were categorised in two major groups of the UNEP Toolkit, i.e. as primary production (a) of ferrous and nonferrous metals, and (b) of cement (natural gas-fired, no waste co-firing). Then, according to the criteria presented in the Toolkit and detailed information gathered from aforementioned questionnaires, subcategories as well as applicable PCDD/Fs emission factors were chosen for different compartments (i.e., air, water, land, products, and residues) (EN 1948-2, 1997).

2.2. Experimental work

2.2.1. Sampling

In this study dust samples were seized after selecting suitable sampling locations, identified after analysis of flow-sheets related to the relevant production and off-gas cleaning plant. The partitioning of dioxins between gas phase and particulates is still unknown. Still, it is plausible that low dust load corresponds with low gas load; thus, the level of dioxins concentration is used as criterion for identifying the locations that need further scrutiny.

2.2.2. Sample pre-treatment, clean-up and analysis

All sample bottles were cleaned thoroughly before using and prepared according to standard method EN-1948. Samples were put in cleaned amber glass bottles, then closed using PTFE-lined screw-caps seals and transferred to the laboratory and stored at sub-ambient temperature (<4 °C)(Kudlak et al., 2007) to avoid losses or prevent contamination.

Sample extraction allows transferring the analytes (PCDD/F or PCB) into the solvent and removing the bulk of sample matrices. The extraction procedure follows Method 1613 (US EPA, 1994a, 1994b). The analysis was conducted by HRGC/HRMS on a 6890 Series gas chromatograph (Agilent, USA) and coupled to a JMS-800D mass spectrometer (JEOL, Japan).

Table 1
PCDD/Fs distribution (% of total TEQ) and total concentration (pg I-TEQ g^{-1} dust) in direct reduction steel plant samples.

Congeners	A	B	C	D
2,3,7,8-TCDD	N.D.	N.D.	5.5	N.D.
1,2,3,7,8-PeCDD	N.D.	N.D.	11.7	N.D.
1,2,3,4,7,8-HxCDD	N.D.	N.D.	2.6	0.4
1,2,3,6,7,8-HxCDD	N.D.	6.5	8.3	1.0
1,2,3,7,8,9-HxCDD	4.5	7.3	5.9	1.0
1,2,3,4,6,7,8-HpCDD	1.9	3.3	5.2	0.4
OCDD	0.6	N.D.	0.7	0.1
2,3,7,8-TCDF	6.5	5.7	4.2	9.4
1,2,3,7,8-PeCDF	5.2	4.9	2.6	3.0
2,3,4,7,8-PeCDF	50.0	43.1	48.8	62.2
1,2,3,4,7,8-HxCDF	9.1	9.8	10.1	7.3
1,2,3,6,7,8-HxCDF	7.1	9.8	7.1	7.0
1,2,3,7,8,9-HxCDF	3.9	4.1	1.1	1.4
2,3,4,6,7,8-HxCDF	9.1	9.8	10.8	6.7
1,2,3,4,6,7,8-HpCDF	1.9	2.4	2.9	1.3
1,2,3,4,7,8,9-HpCDF	0.6	0.8	0.4	0.3
OCDF	0.6	N.D.	0.1	0.1
Sum I-TEQ, % TEQ	100	100	100	100
Total I-TEQ, pg g^{-1}	1.54	1.23	53.5	15.8

N.D. = below the detection limit (estimated at 0.5 pg g^{-1}).

2.2.3. Other characterisation methods

Different methods such as XRF (PhilipsAnalytical V.B., Netherland) and TGA/DTA (STA 409 PC, Netzsch, Germany) were used to characterise the crude samples and investigate the influence of composition and thermal treatment on the selected samples. The results will be interpreted in a dedicated paper.

3. Results and discussions

3.1. First evaluation by using the UNEP Toolkit

The scope of activities of the Iran Mineral Processing Research Center comprehends: integrated iron & steel plant, production of cement, metallurgical cokes, primary aluminium and primary copper metal (no scrap feeding). Some of these activities are unique; others are distributed over several sites. Further analysis leads to (production capacities supplied from the answers to our detailed questionnaires):

(A) Cement industry is classified here as category 4, class 3, subcategory a of the UNEP Toolkit, i.e. Rotary Kiln clinker production, flue gas treatment with Electrostatic Precipitator (ESP) or fabric filter (FF) operating at a temperature above 200 °C. Therefore, the annual release of dioxins and furans from this type of plant (annual production capacity of 1,050,000 tonnes of clinker) was estimated at 0.63 g TEQ $annum^{-1}$ (for the air compartment) based on equations proposed in the Toolkit.
(B) In an integrated iron & steel company the following operations have been identified: primary iron & steel production, foundries, lime production, and continuous steel coil galvanization. Thus, the following plant classes and subcategories were identified:
  - (B1) Steel production, 4.8 M tons of steel per year, subcategory 2-c, Class 1, (due to the additionas coolant to the charge of scrap, possibly contaminated with chlorides);
  - (B2) lime production, 270,000 tons of lime per year, subcategory 4-b, Class 2, (application of fabric filter); and
  - (B3) Continuous coil galvanization plant, 200,000 t/a, subcategory 2-c (Galvanization part), Class 1, (no air pollution control systems).

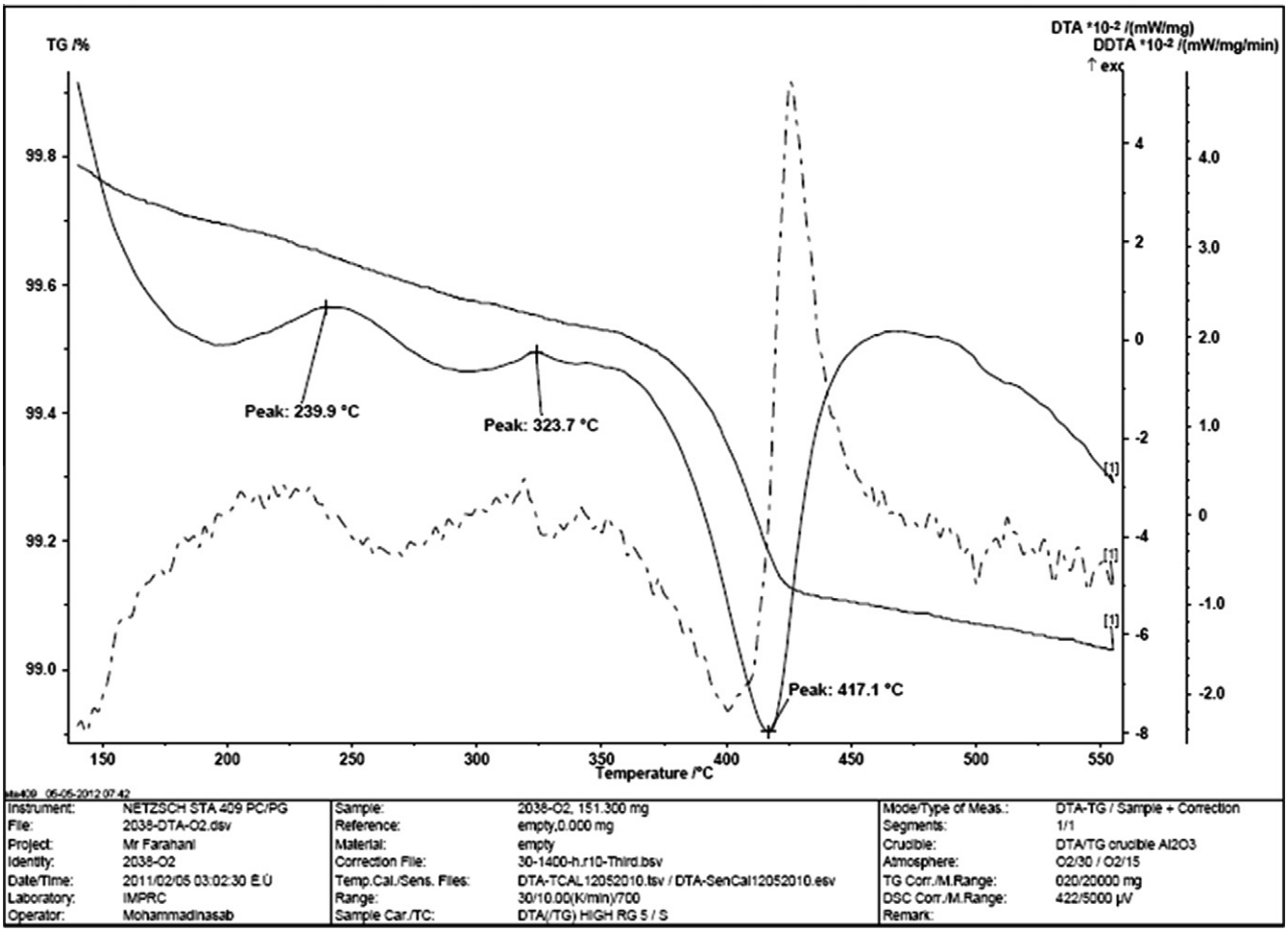

Fig. 1. TGA/DTA graph of sample C, under O_2 atmosphere in a de novo test.

According to the UNEP Toolkit annual releases of dioxins and furans are estimated at 48 g TEQ annum^{-1} and 72 g TEQ annum^{-1} for the compartments air and residues, respectively.

- (B4) Coking chamber plant with the resulting gas transferred to refining and cleaning, classified as Class 2 in subcategory 2-b. According to the Toolkit equations the annual releases of dioxins and furans from this plant, with annual production of 265.7 kt of cokes, were 0.08 and 0.16 g TEQ annum^{-1} for air and water, respectively.

(C) The UNEP Toolkit yields no figures for primary aluminium production, except for its lime production unit. Following classes and subcategories were selected for this plant:

- (C1) Alumina from primary bauxite ores with a production of 280 kt annum^{-1}, subcategory 2-e Class 7.
- (C2) Lime production plant with a capacity of 115.2 kt annum^{-1} of lime, subcategory 4-b, Class 1 (due to absence of any kind of air pollution control system). Emissions of PCDD/F to air amount to 1.15 g TEQ annum^{-1}.

In fact, the UNEP Toolkit does not cover mining operations (e.g. the use of explosives for blasting) and it even expresses explicit caution regarding some data, due to their scarcity. The two integrated iron & steel plants use distinct production processes: the elder employs ore reduction in conventional blast furnace plant as foreseen in the Toolkit, yet the newer plant practices direct reduction of iron ore by steam reformer synthesis gas to pellets. This novel technology remains entirely absent in the Toolkit in particular or in dioxins literature at large; for that reason this plant was selected for further analysis.

A similar situation arises for primary aluminium and copper production: no detailed data is available and presumably emissions remain low, loosely related to the basic process, and barely relevant. As a result the data presented in the Toolkit are approximate, incomplete and at times lacking an appropriately detailed analytical approach in estimating emissions, e.g. in describing the effects of feed impurities, suppression, and abatement techniques.

In metallurgical coking plant the level of diffuse emissions seems determining; the latter is directly related to the frequency and intensity of maintenance activities.

Nevertheless and despite these deficiencies the UNEP Toolkit allows preparing convincing order-of-magnitude estimates, as well as establishing priorities for further work. According to the results obtained by this Toolkit exercise the iron & steel sector emerged as a significant potential source, cement production ranking second, and cokes production third, whereas primary copper and aluminium probably remain negligible as sources of direct dioxins emissions at the stage of primary production. Note that there is no local recycling of scrap or alloying considered. The latter are relevant, major, as well as somewhat unpredictable sources of dioxins (Stieglitz et al., 2003). The highest releases of PCDD/Fs to the air and the residues (wastes) for the selected plants were estimated at ca. 77 and 112 g TEQ per year, respectively.

3.2. Chemical analysis and de novo testing

Dioxins concentrations are expressed in parts per trillion (ppt) or less in technical and environmental samples, whereas other organics are determined in parts per million (ppm) or parts per bil-

Table 2
XRF results for direct reduction steel plant samples.

Sample (%)	L.O.I.	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	ZnO	Cl
A	1.21	4.65	6.18	1.59	6.95	0.44		1.14	29.36	0.66	0.53	44.21	2.32	0.3
B	2.47	5.7	7.2	0.93	4.67	0.64	0.27	1.37	30.84	0.55	0.4	42.46	1.87	0.23
C	9.84	14.95	2.69	0.31	2.49	0.38		5.92	9.28		0.57	38.94	12.48	1.44
D	9.28		3.25	0.29	2.6	0.54		7.49	10.15		0.59	46.54	16.63	1.37

L.O.I. = loss on ignition.

Table 3
ICP–OES results for direct reduction steel plant samples.

Sample (ppm)	Cr	Cu	Ni	V
A	559	265	51	156
B	169	271	50	150
C	379	640	58	169
D	315	450	51	154

lion (ppb). The ultra-trace analysis of dioxins requires sample enrichment using efficient extraction methods and highly selective purification/fractionation techniques. Furthermore, highly sensitive separation equipment (e.g. high resolution gas chromatography–HRGC) with detection level in the ppt range is used to isolate and separate dioxin congeners. Quantification by a high-resolution mass detector (HRMS) requires the use of labelled internal standards (EN 1948-1, 1997).

After joint study of the relevant flow sheets and inspection of the various plants, suitable sampling locations were identified in iron & steel plant and in cement plant. Samples of their raw materials (50 g samples each) and of filter dust (each filter in the plant) were secured. The propensity of these dust samples to form dioxins by the de novo route (low temperature carbon oxidation) was tested. The concentrations of dioxins and Polycyclic Aromatic Hydrocarbons (PAHs) were analysed at Zhejiang University according to the EPA-8290 method to quantify PCDD/Fs concentrations and the results are presented in the following Tables 1 and 4. In order to put PCDD/F emissions in perspective, complementary analyses using methods such as XRF, ICP-OES and TGA/DTA were performed, TGA/DTA of sample C is showed in Fig. 1 and the emission results were statistically evaluated and respectively shown in the below Tables 2, 3 and 5.

HRGS/HRMS analysis shows sample C to be the most contaminated dust sample (Dust collection Bin). Capacity and temperature of this bin were 150 m^3 and 110 °C, respectively. The bin is emptied once every 8 h. Results show that the largest contribution in all samples (43–62%) is due to 2,3,4,7,8-PeCDF. In absolute value the load is relatively low, compared to the sinter route. Further study work is on-going.

This iron & steel plant applies direct reduction, rather than the conventional blast furnace process: natural gas is first converted by steam reforming into reducing gas that in turn directly reduces iron ore into iron pellets.

Concentration and fingerprints have been confronted with other analyses, e.g. Buekens et al. (2001) The TEQ-values have also been statistically correlated with the various composition parameters. Even though the direct reduction data set is rather small the following results are quite in line with other prior and similar exercises in metallurgical systems:

- Strong correlation (r^2): Cu, Ni (>0.97), and V (0.93).
- Some correlation (r^2): Cl, L.O.I. (0.81), and Na (0.78).
- Weak correlation: K (0.64), Zn (0.62), and Mn (0.55).
- No correlation: Cr (0.06).
- Weak negative correlation: SiO_2 (−0.71), Fe_2O_3, Al_2O_3 (−0.69), and P_2O_5 (−0.68).
- Negative correlation: SO_3 (−0.86), Mg (−0.83), Ca (−0.8), and Ti (−0.77).

The two more heavily loaded samples are internally strongly correlated (0.98). The two others carry an almost negligible TEQ load.

Since direct reduction has never been described from a viewpoint of dioxins generation, it seems worthwhile briefly describing these findings.

The graphs showing TEQ as a function of copper (Fig. 2a) or chlorine (not shown) suggest an at least linear relationship between these variables. Conversely, Figs. 2b and 2c suggest a hyperbolic relationship between TEQ and MgO or SO_3.

Table 4
PCDD/Fs distribution (% of total TEQ) and total concentration (pg I-TEQ g^{-1} dust) in the samples of cement factory.

Congeners	Sample from various cement plants						
	A	B	C	D	E	F	G
2,3,7,8-TCDD	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,2,3,7,8-PeCDD	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,2,3,4,7,8-HxCDD	0.0	0.0	0.0	0.0	0.0	3.6	0.0
1,2,3,6,7,8-HxCDD	0.0	0.0	0.0	0.0	0.0	5.1	0.0
1,2,3,7,8,9-HxCDD	6.1	8.6	4.3	38.2	5.7	8.0	6.1
1,2,3,4,6,7,8-HpCDD	0.9	1.7	1.6	1.5	1.4	1.5	1.0
OCDD	0.0	0.0	0.4	0.0	0.0	0.0	0.0
2,3,7,8-TCDF	14.8	8.6	5.1	6.9	5.0	3.6	7.1
1,2,3,7,8-PeCDF	3.5	3.4	1.6	2.3	2.1	3.6	3.1
2,3,4,7,8-PeCDF	46.1	45.7	20.6	49.6	52.1	50.4	54.1
1,2,3,4,7,8-HxCDF	6.1	9.5	4.3	6.9	8.6	5.1	8.2
1,2,3,6,7,8-HxCDF	7.0	7.8	3.5	9.2	6.4	3.6	5.1
1,2,3,7,8,9-HxCDF	3.5	4.3	1.9	6.9	3.6	3.6	4.1
2,3,4,6,7,8-HxCDF	9.6	8.6	0.4	9.9	10.0	8.0	8.2
1,2,3,4,6,7,8-HpCDF	1.7	2.6	1.2	2.3	2.9	1.5	2.0
1,2,3,4,7,8,9-HpCDF	0.9	0.9	0.4	0.8	0.7	2.2	0.0
OCDF	0.0	0.0	0.0	0.0	0.7	0.0	0.0
Total I-TEQ, %	100	100	100	100	100	100	100
Total I-TEQ, pg TEQ g^{-1}	1.15	1.16	2.57	1.31	1.4	1.37	0.98

Table 5
XRF results for cement samples.

Sample/%	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	ZnO	Cl	SrO
A′	1.83	0.24	2.24	4.48	19.5	0.08	2.5	0.73	63.1	0.36	4.78			0.09
B′	0.3	0.2	2.35	4.28	19.3	0.09	1.9	0.75	65.5	0.33	4.83			0.09
C′	0.13	0.4	2.22	3.98	18.9	0.07	1.0	1.32	68.1		3.87		0.1	
D′	0.36	0.38	2.34	3.97	19.6	0.08	1.0	1.37	66.6		4.09		0.1	0.08
E′	6.7	0.22	2.2	3.94	17.9	0.07	2.3	0.63	60.6	0.4	4.95			0.09
F′	1.92	0.26	2.28	4.21	19.4	0.06	2.5	0.7	64.3		4.26			0.09
G′	0.43	2.47	2.2	3.25	16.4	0.12		1.62	67.2	0.36	5.36	0.22	0.3	0.09

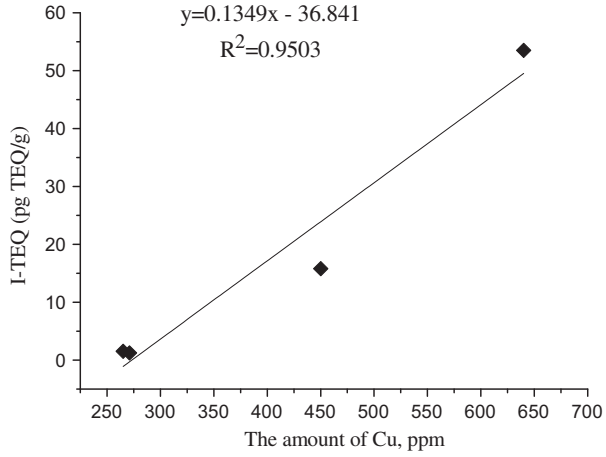

Fig. 2a. TEQ plotted as a function of the amount of copper (in ppm) in the dust samples.

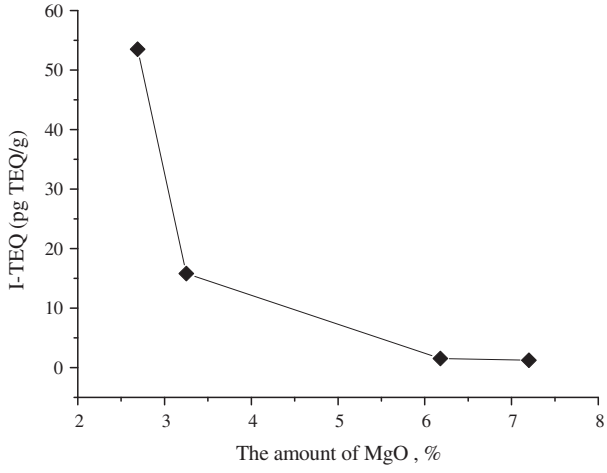

Fig. 2b. TEQ plotted as a function of the amount of magnesium (in wt.%, analysed as MgO) in the dust samples.

In the case of cement there are only very few variables showing any correlation at all with TEQ, only exceptions being Sr ($r^2 = -0.96$), Fe_2O_3 (−0.72), TiO_2 (−0.57). This absence of correlation is ascribed to the conjunction of very low TEQ-values and the main factors affecting the formation of dioxins, such as catalysts (volatile metals), organics, and halogens.

In cement samples the dioxins load is unusually low, ranging between 1 and 2.6 pg TEQ g^{-1}. This is even lower than typical house dust values. Stieglitz et al. (2003) cite values of 0.4 ng g^{-1} PCDD and 0.98 ng g^{-1} PCDF, yet no de novo formation activity. Lime and sulphur both suppress the formation of PCDD/Fs. The most toxic congener, 2,3,7,8-TCDD, always remains below D.L.

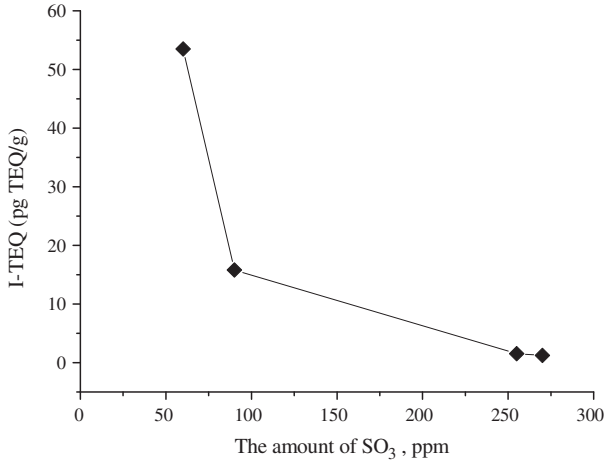

Fig. 2c. TEQ plotted as a function of the amount of sulphur (in ppm, analysed as SO_3) in the dust samples.

Apparently, the cement sector and even the integrated iron & steel plant (direct reduction) are rather small sources of dioxins, especially in these samples from Iranian industry.

Also, the emissions of PCDD/Fs by these plants in Iran are lower than permitted levels and TDI (Tolerable Daily Intake) for people in the most polluted point in steel plant is:

$$\begin{aligned} \mathrm{DI} &= \mathrm{TD} \cdot D \cdot R \cdot W \cdot N/365/\mathrm{BW}/\mathrm{PF} \\ &= 100\ \mathrm{mg\ m^{-3}} * 53\ \mathrm{pg\ g^{-1}} * 1\ \mathrm{m^3\ h^{-1}} * 4 * 250 * 10^{-3}/356/60 \\ &= 0.28\ \mathrm{pg\ kg^{-1}\ d^{-1}} \end{aligned}$$

where DI is the dioxin intake; TD the total dust exposure concentration (mg m^{-3}); D the dioxin concentration in dust (ng TEQ g^{-1}); R the respiratory ventilation ($m^3\ h^{-1}$); W the working duration (h/once); N the number of times annum^{-1} (200 for daily operation, 4 for periodic maintenance); BW the body weight (kg); and PF is the protection factor.

4. Conclusions

This study refers to the application of the UNEP Toolkit to the relevant factories operating for the Iranian Mines and Mining Industries. Estimates were generated for integrated iron & steel plant (cokes production included), the cement sector, as well as primary aluminium and copper production. The UNEP Toolkit does not present emission values either for the latter two primary metal industries, or for direct reduction as an innovative method for steel production.

The dioxins emissions from eight major metallurgical and cement plants were estimated. Both ferrous and non-ferrous metallurgical processes potentially represent a serious source of PCDD and PCDF emissions. Steel plant and cement plant were selected for sampling dust at all accessible process locations and for

analysis of the related PCDD and PCDF emissions. Samples were taken from cement plant and also in an integrated iron & steel plant practising direct reduction. All samples were physically and chemically characterised (test results will be published elsewhere), tested by TGA/DTA for establishing the extent of catalytic carbon oxidation activity at low temperature (responsible for de novo synthesis) and analysed for dioxins and furans.

Dust samples were analysed because PCDD/Fs mainly attach to the dust surface. Sampling in the steel plant was conducted while intentionally polluted scrap was charged (worst case conditions), so that in normal condition this emission is presumably much lower. As a consequence the emissions of PCDD/F from these plants are lower than permitted levels and TDI for people in the most polluted point in steel plant is 0.28 pg kg^{-1} d^{-1}. These studies are still on-going.

Acknowledgements

Authors thank the Iranian Mines and Mining Industries Development and Renovation (IMIDRO) for financially supporting this work.

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